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U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5)

08/793966

INTERNATIONAL APPLICATION NO.
PCT/EP95/02722INTERNATIONAL FILING DATE
July 12, 1995PRIORITY DATE CLAIMED
Sept 9, 1994/Mar 10, 1995

TITLE OF INVENTION

BIOLOGICALLY DEGRADABLE POLYESTER AND WORKING MATERIAL CONSISTING THEREOF

APPLICANT(S) FOR DO/EO/US

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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US)
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☐ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A FIRST preliminary amendment.
☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information: Verified Statement Claiming Small Entity Status
-- Small Business

"Express Mail" Mailing Label No.: EH 951 470 643 USDate of Deposit: March 10, 1997

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 C.F.R. 1.10 on the date indicated above and is addressed to the Assistant Commissioner for Patents, BOX PCT, Washington D.C. 20231

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PCT/EP95/02722

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17. ☐ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):**

Search Report has been prepared by the EPO or JPO..... \$910.00

International preliminary examination fee paid to USPTO (37 CFR 1.482)
..... \$700.00No international preliminary examination fee paid to USPTO (37 CFR 1.482)
but international search fee paid to USPTO (37 CFR 1.445(a)(2)).. \$770.00Neither international preliminary examination fee (37 CFR 1.482) nor
international search fee (37 CFR 1.445(a)(2)) paid to USPTO..... \$1040.00International preliminary examination fee paid to USPTO (37 CFR 1.482)
and all claims satisfied provisions of PCT Article 33(2)-(4)..... \$96.00
ENTER APPROPRIATE BASIC FEE AMOUNT =Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE
Total claims	6 -20 =	0	X \$22.00
Independent claims	2 -3 =	0	X \$80.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+\$260.00

TOTAL OF ABOVE CALCULATIONS =Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity Statement
must also be filed (Note 37 CFR 1.9, 1.27, 1.28).**SUBTOTAL =**Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(f)). +**TOTAL NATIONAL FEE =**Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +**TOTAL FEES ENCLOSED =**Amount to be:
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charged \$a. ☒ A check in the amount of \$ 495.00 to cover the above fees is enclosed.b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.
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overpayment to Deposit Account No. 02-3978. A duplicate copy of this sheet is enclosed.**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

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The invention relates to biodegradable polyesters (particularly in the form of a raw material or working material), and to materials made from the polyester.

Polyesters belong to prior art. For example, EP-A-0 007 445 describes a mixed polyester on the basis of butanediol-1,4 and terephthalic acid, 10 to 30 mol-% of the terephthalic acid being replaced by a mixture of 20 to 80 mol-% adipic acid, 10 to 60 mol-% glutaric acid and 10 to 40 mol-% succinic acid, and in which the percentage numbers add up to 100. These known mixed polyesters are provided for producing moulded parts by injection moulding or extrusion. Such mixed polyesters however are not biodegradable, which might be ascribed, (as will become apparent from later statements), to the high minimum percentage of 70 mol-% of terephthalic acid as an aromatic polycarboxylic acid. Further, EP-A-0 028 587 describes copolyesters of 40 to 85 mol-% terephthalic acid (which can be replaced up to 50% by other dicarboxylic acids, for example sebacic acid), 60 to 15 mol-% adipic acid and C2-6 alkanediolene, such as butyleneglycol. These known copolyesters are provided as hot-melt adhesives or powdery covering means, so that there is no question of their biodegradability. The document EP-A-0 028 687 refers to much older prior art for the production and use of these known copolyesters.

It is known that specific polymeric materials can undergo biodegradation. Principally in this case there are to be

named materials which are obtained from naturally occurring polymers directly or after modification, for example polyhydroxalkanoates such as polyhydroxybutyrate, plastic cellulose esters, plastic starches, chitosan and pullulan. A concerted variation of the polymer composition and of the structure, as is desirable from the standpoint of utilisation of polymers, may only be achieved with difficulty and frequently to a very restricted degree due to the natural synthesis procedure.

On the other hand, many synthetic polymers are not or only extremely slowly attacked by micro-organisms. It is mainly synthetic polymers containing hetero atoms in the main chain which are regarded as being potentially biodegradable. An important class within these materials is represented by the polyesters. Synthetic polyesters, which contain only aliphatic monomers, do in fact have relatively good biodegradability but, due to their material properties, may only be used to a very restricted degree; see Witt et al. in *Macrom. Chem. Phys.*, 195 (1994) 793-802. On the other hand, aromatic polyesters, which have good material properties, are not biodegradable.

An object of the present invention is to synthesise copolymers (particularly in the form of a raw material or working material), which simultaneously have good biodegradability and good thermal and mechanical properties. This object is achieved in that synthetic

copolymers with a specific composition are produced.

Thus the object underlying the invention is achieved by a biodegradable polyester which is degraded in a naturally environment by the action of micro-organisms, for example according to DIN 93739D or ASTM D5338-92, the polyester being characterised in that it has been produced from an aliphatic polyol and an aromatic polycarboxylic acid and also simultaneously from an aliphatic polycarboxylic acid as a monomer component, and has constitutional repeater units or returning units, which

(1) consist on the one hand of polyol and aromatic polycarboxylic acid and

(2) on the other hand consist of polyol and aliphatic polycarboxylic acid,

more than 90% of the units according to (1) being linked with no or at most one further unit according to (1) directly.

According to the invention it has become surprisingly apparent that it is possible to synthesise copolyesters from diols and aromatic and aliphatic dicarboxylic acids which, high in material properties which are relevant to the technology of the application, are also subject to biodegradation.

The polyester according to the invention can have a molecular weight of 1000 to 70000 g/mol.

Further, the polyester according to the invention can have a melting point of 40 to 150°C and in particular 90 to 150°C.

The polyester according to the invention may also have been condensed from

- aliphatic C2-6-diol, preferably 1, 2-ethandiol, 1, 2 - propanediol, 1, 3-propanediol, 1, 4-butanediol, 2, 3-butanediol or 1, 6-hexanediol
- from an aromatic dicarboxylic acid, preferably terphthalic acid, and
- an aliphatic C2-10-dicarboxylic acid, preferably adipic acid or sebacic acid.

Whereas, when there are small proportions of aromatic components, no or only a slight improvement in the material properties of the polymers is to be observed, when there are medium proportions of 3 to 65 and especially 35 to 55 mol-% aromatic components of the dicarboxylic acid, a drastic increase, particularly of the melting point, is observed. Such copolyester can show clear weight losses in environments such as compost or soil within 2 to 3 months.

Accordingly, the invention further relates to a polyester with a proportion, based on an aromatic dicarboxylic acid as a monomer component, of 3 to 65 and especially 3 to 55 mol-% (related to the overall acid content).

A further object of the present invention is to provide a raw material or working material which at the same time is biodegradable and has good thermal and mechanical properties. This object is achieved according to the invention by a material of a biodegradable polyester according to the invention, the material existing in the form of flat material, particularly films, single filaments, filamentary material or moulded parts, particularly injection moulded, extruded or foamed moulded parts. Filamentary material can be present in the form of fibres, felt or textile. Composite material may form the material according to the invention.

Applications of the material according to the invention are enumerated in the following, viz.:

- films, particularly packing films, for example for packing fresh goods in retail, or for ready packed goods in retail, such as secondary packaging (bundles of individual packages) "skin packaging" (for small articles such for example as nails), blister packs (films on cardboard carriers, particularly for sweets) protective packagings or transparent films, for example in

floristry; compost bags, particularly for domestic wastes (for example 10 l) or garden wastes (for example 100 l); films in medical use, particularly for or as disposable clothing or gloves; films as or in the form of baby nappies; "big bags", particularly large volume sacks, for example for bulk materials such as fertilisers or feeds; covering films, for example in agriculture; labels; or weather balloons; transport packages, clothes bags, building films or bedding underlays;

- fibres, felts or textiles, particularly binding material for landscaping or in floristry; tree nets, particularly for protecting cultivated plants from birds; cover nets for ground areas, for example against soil erosion; nets for foodstuffs packagings, for example for vegetables or fruit, nets for the sale of trees or shrubs, such as Christmas trees, fishing nets; cloths in household use, such as cleaning cloths; nappy inserts; fleeces in the hygiene and cosmetics field; fleeces in the medical field; mist removing filters; automobile interior filters, filters for the foodstuffs field, particularly for breweries, filters for aquaria and ponds;

- extruded moulded parts, particularly disposable crockery; foodstuffs packaging, for example yoghurt cartons, bottles or tubes; cosmetic packagings, for examples bottles or tubes; bags closures, disposable articles in the medical field, for example syringes or

spatulas; plastics articles for firework bodies, plastic ammunition, for example for defence purposes; cemetery and funeral equipment, for example funeral wreaths, funeral lights or coffin applications; golf tees, pellets for controlled release, for example for fertilisers or plant protection; carrier members for drinking water preparations, plant pots, support rods, for example for gardens; support members for soil, particularly in the case of suspended plants;

- composite materials, particularly drinks packagings, composite paper cartons, for example for snacks, powdered milk or raisins, coated papers, for example with improved moisture resistance; cloths, for example made of fibres according to the invention in conjunction with natural fibres; compressed fibre mats, for example as "adhesives", also in the form of plant pots or for automobile interior trims, composite fibres, particularly furniture parts or supportive automobile interior trims;

- foamed materials, particularly packaging chips; foamed packaging bodies, plant bowls, floor ventilators, disposable crockery, packaging trays, particularly for meat, fruit, eggs or pills, or upholstery material.

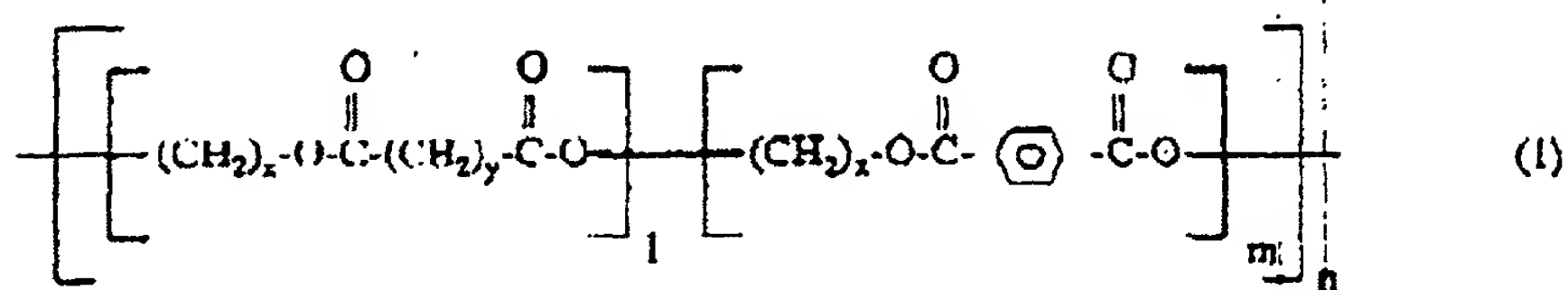
The invention will be described in more detail in the following, particularly by means of examples, discussing the degradability of the polyesters according to the invention.

The answer to the question of the cause of biodegradation of specially composed copolyesters synthesised from aromatic and aliphatic dicarboxylic acids was found by investigating the biological metabolic capacity of model oligomers. Oligomers, for example of terephthalic acid and 1, 3-propanediol are only partly degraded, and a sharp distinction was revealed as regards the lengths of the oligomers. Insight into the degree of metabolisation of such copolymers in natural environments such as compost or earth was gained from the degradation behaviour of the model oligomers and of the calculated or measured monomer distribution in the copolymer.

1. Synthesis of polycondensates

For the production of statistical polyester-copolymer by condensation of aliphatic diols with aliphatic and aromatic dicarboxylic acids, the monomer components listed in Table 1 are suitable, which are available either by known petrochemical processes in large volumes and in a cost-effective manner, or are at least partly accessible by means of biotechnological processes, from sustainable raw materials (1, 3-propanediol, 2, 3-butanediol, adipic and sebacic acid).

Synthesis of the polyester-copolymer was effected as shown in Examples 1 to 9, and leads to polycondensates of the structural formula 1.



Polyester-Copolymer

Polyester-copolymers.

Table 1: Components for Polyester-Copolymers

Diols	Dicarboxylic Acid
1,2-ethanediol	adipic acid
1,3-propanediol	sebacic acid
1,4-butanediol	terephthalic acid
2,3-butanediol	
1,6-hexanediol	

Examples of the polycondensates relevant to the invention, whose average molecular weights, melting points and film properties are listed in Table 2.

Table 2: Properties of typical synthesised polyester-copolymers of the general composition according to equation (1)

ETA ($x = 2$, $y = 4$): Poly(dimethylene-hexanedioate-co-dimethylene-terephthalate)

PTA ($x = 3$, $y = 4$): Poly[(trimethylene-hexanedioate-co-trimethylene terephthalate)]

PTS ($x = 3, y = 8$): Poly[(trimethylene-decanedioate-co-trimethylene-terephthalate)]

BTA ($x = 4, y = 4$): Poly[(tetramethylene-hexanedioate-co-tetramethylene-terephthalate)]

Polymer*	Consistency	Mw**	Tm	
Film		g/mol	°C	Properties
ETA (38/62)	fibre	30,000	87	flexible, opaque
ETA (44/56)	fibre	39,000	135	flexible, opaque
PTA (5/95)	powder	47,000	50	fragile, opaque
PTA (17/83)	powder	24,000	44	fragile, opaque
PTA (23/77)	powder	40,000	40	flexible, opaque
PTA (39/61)	fibre	51,000	96	flexible, opaque
PTA (43/57)	fibre	40,000	119	flexible, opaque
PTS (3/97)	powder	17,500	56	fragile, opaque
PTS (7/93)	powder	22,000	55	fragile, opaque
PTS (9/91)	powder	23,000	48	fragile, opaque
PTS (29/71)	powder	25,000	40	fragile, opaque
PTS (41/59)	fibre	53,500	95	flexible, opaque
PTS (56/44)	fibre	49,000	139	flexible, transparent
BTA (34/66)	fibre	47,000	88	flexible, opaque
BTA (42/58)	fibre	46,000	117	flexible, opaque
BTA (51/49)	fibre	50,000	142	flexible, opaque

* in brackets: molar ratio of aromatic to aliphatic dicarboxylic acid

** determined via GPC measurement, relating to polystyrol standard

E: dimethylene T: terephthalic acid A: adipic acid
P: trimethylene S: sebacic acid
B: tetramethylene

2. Thermal properties

The thermal properties are characterised by the melting points (see Table 2). For the case of the copolyesters with 1, 3-propanediol and diol components such as PTA and PTS, which due to their C number adopt a central position, the melting behaviour was more closely investigated in dependence on the proportion of terephthalic acid. Up to a terephthalic acid content of about 30 mol-% (relative to the acid proportion in the copolyester) there exist melting points and material properties which correspond to those of pure aliphatic polyesters (e.g. SP36; saturated polyester of 1, 3-propanediol and adipic acid, SP 310; saturated polyester of 1, 3-propanedio and sebacic acid). The purely aliphatic polyesters proved to be biodegradable, but have a large deficit in material properties (Witt, Mueller, Augusta, Widdeke and Deckwer, Macrom. Chem. Phys. 195 (1994), 793, 802). As Figure 1 shows, the melting points and material properties for the investigated PTA and PTS copolyesters however increase rapidly at a terephthalic acid content (T-content) of about 35 mol-%. As is further shown, there results for such copolyester systems a narrow optimum range between degradability on the one hand and material properties on the other hand, which lies at T-contents of about 35 to 50 mol-%. Here the

bottom proportion arises from the minimum requirements for utility properties (such for example as melting points of at least 90°C, and adequate film and fibre properties) the top component from the requirement for biodegradability (see Sections 4 and 5).

3. Stability against Hydrolysis

In order clearly to assess the biodegradation tests, tests were carried out to see how far the synthesised polyester copolymers are subject to hydrolytic degradation. These investigations, as shown in Example 10, were carried out with the exclusion of micro-organisms at ambient temperature and 60°C.

After three months of action at ambient temperature no weight losses or other measurable degradation phenomena resulted in films of PTA and PTS copolyesters.

In the tests at 60°C, after 10 weeks of action slight or minimal weight losses resulted. These amounted for copolyester PTS (41/59) and PTS (56/44) about 0.0% and for the copolyesters PTA (39,61) and PTA (43/57) about 3.5 or 6%. Thus in the PTA esters with adipic acid as an aliphatic dicarboxylic acid component a more intense chemical hydrolysis was observed in the period of time tested than with the PTS copolyesters with sebacic acid

as a dicarboxylic acid component. As is shown in the following section, the weight loss by hydrolysis is however only a fraction of that achieved during biodegradation at 60°C (composting).

4. Biodegradation

Experiments in the aquatic system

Polyester films (25 mm , 100 m thickness) were treated in 100 ml liquid volume at 25°C, stirred and with an air supply. A corresponding mineral salt medium and an earth or compost eluate were added. As Figure 2 shows, PTA and PTS copolyesters were well degraded down to a proportion of terephthalic acid of 30% in the indicated aquatic system. Degradation of the statistic copolyesters with terephthalic acid components of > 30 mol-% (relative to the acid content) were however not observed in the aquatic system. Clearly in this case the presence of the microbial mixed culture and of the mineral salts is insufficient for a microbial degradation in the period of time observed.

Degradation Experiments with Burial in Earth

As described in Example 11, degradation experiments by means of burial in earth were carried out according to DIN 53739D at a relative humidity of 60% and at ambient

temperature. The results of these experiments are illustrated in Figure 3. From this it is to be seen that the polyester copolymers with low proportions of terephthalic acid (PTS (41/59) and PTA (39/61)) could no longer be isolated after 7 or 8 weeks.

For PTA (43/57) a weight loss of 14% became apparent after a period of 8 weeks. On the other hand, no weight loss and no optical clues to microbial attack could be seen for PTS (56/44).

Composting at 60°C

In addition to the earth burial test, degradation in compost at 60°C and 60% relative humidity was tested. In this case a compost of green wastes from the post-fermentation stage of the composting system Watenbuttel (Braunschweig) the results, in dependence on the treatment time, are shown in Figure 4. After 6 to 7 weeks, the statistical copolyesters with adipic acid (PTA) were no longer to be isolated from the compost. The PTS copolyesters are also biologically attacked and reveal significant weight losses which are considerably greater than would be expected with purely chemical hydrolysis. For PTS (41/59), the weight loss is about 50% and for PTS (56/44) at about 20% after 10 weeks treatment time in all.

5. Use of Model Oligomers with Terephthalic Acid as an Acid Component

Most of the known polyesters with aliphatic acids can be fully biodegraded. The degradation results shown under 4 show that this is also possible if the proportion of aromatic diocarboxylic acid does not exceed a specific value. In order to gain insight into which structural unit with aromatic dicarboxylic acids still are degraded, experiments were carried out with model oligomers, 1, 3 propanediol, due to its central position, and terephthalic acid again being used. The synthesis of these oligo-trimethylene terethphalates or poly-trimethylene terethphalates (PTMT) is described in Example 12. In Table 3 the average molecular weights (determined by GPC with polystyrol as standard) and their melting points are given.

Table 3: Aromatic PTMT Oligomers by 1,3-propanediol Excess

Oligomer	M_w [g/mol]	T_m [°C]	1,3 Propandiol Überschuß [mol %]
PTMT 1	2630	194	20
PTMT 2	2010	184	50
PTMT 3	1680	176	100

These model oligomers were investigated in the modified Sturm test with 1% compost eluate-as inoculum, the biopolymer polyhydroxybutyrate/-valerate (PHR/V) being

used for comparison purposes. The results are listed in the form of the CO₂ development in dependence on the observation time, in Figure 5. It will be recognised from this that, as the average molecular weight of the aromatic oligomers decreases, the degradable proportion rises significantly.

The partial degradation was achieved after less than 20 days. After this time the CO₂ development increases only slightly. It is notable that the adaptation time in all cases is even shorter than with the degradation of PIB/V. Table 4 shows the C end results which in principle are well achieved. In order to establish the C end results, protein in the biomass according to Lowry was determined and residual polymer was detected after destruction of the biomass by hypochlorite. The dissolved components are detected by determination of the chemical oxygen requirement.

Table 4: C end result of the aromatic PTMT oligomers after microbial degradation in the Sturm test (4 weeks, 25°C, 1% by volume compost eluate, PHB/V serving as a "degradation standard")

Carbon (% of theoretical) determined via

Oligomer	Kohlenstoff (% der Theorie) ermittelt über				
	a) CO ₂ -Entwicklung	b) Biomasse	c) Lösliche Komponenten (CSB)	Rest- polymer	Σ a,b,c + Respolymer
PTMT 1	10,2	< 0,1	0,0	87,1	97,3
PTMT 2	16,1	< 0,1	2,5	78,3	97,4
PTMT 3	23,2	< 0,1	4,0	74,9	102,2
PHB/V *	54,5	46,6	3,8	0,0	104,9

oligomer CO2 development Biomass soluble components (CSB) residual polymer a,b,c+ residual polymer

The distribution of the oligomers in the PTMT 1 - 3 was investigated by gel permeation chromatography before and after degradation. The molecular weights Mps obtained from GPC relate to polystyrol as a calibration standard. The average difference of these values (= 377, except for the peak "CD") relative to the mass of the constitutional repeater unit of the PTMT oligomers (= 206) gives a factor of 0.55. By multiplication of Mps1 with this factor there is obtained MGPC. With the aid of mass spectroscopy, after GPC fractionation, there was obtained a total association of all polymerisation products (MH+MS). The peak association thus obtained is given in Table 5, and Table 6 shows the chromatogram for the synthesis oligomer mixture PTMT3 before its use in degradation tests. The peak CD occurring after an elution time of 8.84 minutes relates to the cyclic dimer, which occurs as a by-product of PTMT synthesis.

Table 5: Association of the Mass Peaks in the GP Chromatogram

Peak	M_{PS} nach GPC bezogen auf PS-Standard [g/mol]	M_{GPC} [g/mol] (= $M_{PS}/0,55$)	M_{th} [g/mol]	$MH^{+}MS$: aus Massen- spektrometrie [g/mol]
1	420	231	282	283
CD	(540)	(297)	412	413
2	780	429	488	489
3	1160	638	694	695
4	1550	853	900	901

MPS acc. GPC rel.

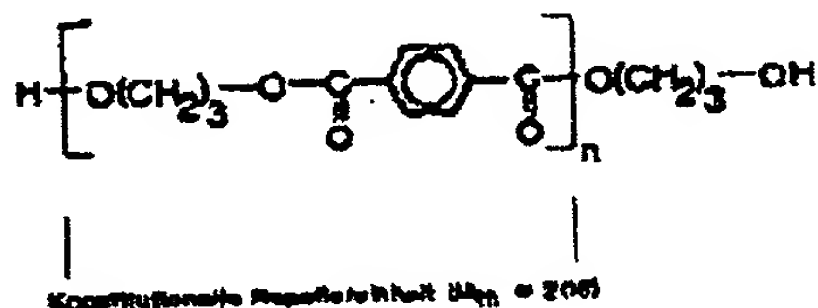
MH+MS from

PS standard [g/mol]

mass spectrography

[g/mol]

Figure 7 now shows the GP chromatograms of PTMT 1 - 3 before and after degradation in the Sturm test. From this it can be seen that the partially degraded components always involve the same peaks (n - 1 and 2). The degradable constitutional repeater unit is thus

Constitutional Repeater Unit ($M_{th} = 206$)

with $n \geq 2$. As the proportion of these degradable repeater units ($n \geq 2$) in the oligomer increases with decreasing molecular weight, the proportion of the degraded oligomeric mass also increases (see Figure 5 and CO₂ development in Table 4). Totally coincident chromatograms were revealed by a repetition of the

degradation tests with 1 and 10 volume-% inoculum over a period of 8 weeks at 30°C, in the GPC tests before and after degradation. Even with composting at 60°C, no degradation of aromatic sequences with $n = 3$ of the PTMT oligomers was observed. Thus, in the period observed (8 weeks) and under the given conditions, degradation of aromatic sequences with $n = 3$ can be excluded. The given optimal range of 35 - 50 mol-% T content in the acid proportion thus cannot be displaced towards greater T contents without at the same time increasing the proportion of non-degradable aromatic sequences in the copolyester.

As statistical polyesters and not strictly alternately structured polyesters are involved in PTA and PTS copolycondensates, the statistical distribution in dependence on the monomer composition was calculated in order to assess the degree of biodegradability. The theoretical dependence of the distribution of sequence lengths in $n > 2$ in the monomer concentration (T content) is shown in Figure 8. For the statistical copolyesters used in the degradation tests there result, upon conversion into percentages by weight, the components of aromatic block lengths given in Table 6. From this it is to be seen that the proportion of degradable aromatic constitutional repeater units in the copolymer lies at over 90%, if the proportion of terephthalic acid in the acid proportion does not rise above 50%.

Table 6: Proportion of Aromatic Sequences with n = 3 in Polyester Copolymers

Table 6: Proportion of Aromatic Sequences with n = 3 in Polyester Copolymers

Polyester	Gew. % an aromatischen 1- und 2er-Sequenzen im Polymer	Gew. % an aromatischen Sequenzen ≥ 3 im Polymer
PTA (39/61)	94,3	5,7
PTA (43/57)	92,3	7,7
PTS (41/59)	94,1	5,9
PTS (56/44)	84,7	15,3

weight % of aromatic 1-

weight % of aromatic

and 2-sequences in polymer

sequences ≥ 3 in polymer

Examples

Example 1

Synthesis of poly[(trimethylene hexanedioate)-co-trimethylene terephthalate)] PTA(39/61)

0.207 mol 1,3 propanediol, 0.074 mol

dimethylterephthalate (DMT), 0.112 mol adipic acid and

0.04 g zinc acetate dihydrate as catalyst are

polycondensed by condensation in the melt. A 100 ml

three-necked flask with vacuum stirring system serves as

a polymerisation reactor. Nitrogen feed and condenser.

The reaction flask is rinsed with nitrogen and, being

stirred, is heated within 10 h gradually to 170°C. In

this case the greater part of the condensate forming

condenses off. Then the pressure is gradually reduced to

0.01 mbar, and condensed, with GPC monitoring, to the

desired molecular weight of $M_w = 30,000 - 70,000$ g/mol. Diol inserted as an excess also condenses off. The copolyester is cooled under vacuum, repeatedly dissolved in chloroform and precipitated in ice-cold methanol (industrial purity) and then dried for 24 h in vacuum.

Example 2

Synthesis of poly[(trimethylene hexanedioate)-co-trimethylene terephthalate] PTA(43/57)

0.207 mol 1,3 propanediol, 0.093 mol

dimethylterephthalate (DMT), 0.093 mol adipic acid and

0.04 g zinc acetate dihydrate are condensed as in Example 1.

Example 3

Synthesis of poly[(trimethylene decandioate)-co-trimethylene terephthalate] PTS(41/59)

0.207 mol propanediol, 0.074 mol dimethylterephthalate

(DMT), 0.112 mol sebacic acid and 0.05 g zinc acetate

dihydrate are condensed as in Example 1.

Example 4

synthesis of poly[(trimethylene decandioate)-co-trimethylene terephthalate] PTS(56/44)

0.207 mol 1,3 propanediol, 0.093 mol

dimethylterephthalate (DMT), 0.093 mol sebacic acid and

0.05 g zinc acetate dihydrate are condensed as in Example

1.

Example 5

Synthesis of poly[(ethylene hexanedioate)-co-ethylene terephthalate)]ETA (38/63)

0.220 mol 1,2-ethanediol, 0.080 mol dimethylterephthalate, (DMT), 0.112 mol adipic acid and 0.04 g zinc acetate dihydrate are condensed as in Example 1.

Example 6

synthesis of poly[(ethylene hexanedioate)-co-ethylene terephthalate)]ETA(44/56)

0.022 mol 1,2-ethanediol, 0.100 mol dimethylterephthalate (DMT), 0.100 mol adipic acid and 0.04 g zinc acetate dihydrate are condensed as in Example 1.

Example 7

Synthesis of poly[(tetramethylene hexanedioate)-co-tetramethylene terephthalate)]BTA(34/66)

0.165 mol 1,4 butanediol, 0.045 mol dimethylterephthalate (DMT), 0.105 mol adipic acid and 0.04 g zinc acetate dihydrate are condensed as in Example 1.

Example 8

synthesis of poly[(tetramethylene hexanedioate)-co-tetramethylene terephthalate)] BTA 12/58)

0.165 mol 1,4 butanediol, 0.060 mol dimethylterephthalate (DMT), 0.090 adipic acid and 0.04 g zinc acetate dihydrate are condensed as in Example 1.

Example 9

Synthesis of poly[(tetramethylene hexanedioate)-co-tetramethylene terephthalate]BTA 51/19)

0.165 mol 1,4 butanediol, 0.075 mol dimethylterephthalate (DMT), 0.075 mol adipic acid and 0.04 g zinc acetate dihydrate are condensed as in Example 1.

Example 10

In the statistical copolyesters produces in Examples 1 - 4 the hydrolysis resistance at ambient temperature is determined. Polyester films are sterilised with ethanol and agitated in sterile water at ambient temperature (150 rpm). In the period investigated of 3 months no alterations as regards weight loss and chain fractures (determined by GPC measurements) were observed. In addition, the hydrolysis resistance was determined in the statistical copolyesters produced in Examples 1 - 4 at 60°C. Polyester films are sterilised with ethanol and agitated at 60°C in sterile water (150 rpm). The statistical copolyesters PTS(41/59) and PTS(56/44) reveal no weight losses after 10 weeks, PTA(39/61) and PTA(43/57) a weight loss of 3.5% and 6% respectively.

Example 11

The degradability of the statistical copolyesters is tested in an earth burial experiment (DIN 53739D). Sample members with a wall thickness of 100 mm and diameter 25mm are welded to form polyethylene nets, and buried in soil

with a relative humidity of 60%. The experiment is carried out at about 20°C. At intervals of time the mass loss of the samples is determined, i.e. the percentage loss in weight of the polyester film. For this purpose at each time-interval a sample is removed, washed with distilled water and dried for 24h in vacuum. This removed sample is not than re-buried in the burial experiment, but is available for analytical investigations. The experiment was carried out with the following polymeric materials: PTA(39/61), PTA(43/57), PTS(41/57) and PTS(56/44). The results are to be seen in Fig. 3.

In addition, the degradability of the statistical copolyesters are tested by composting at 60°C and 60% relative humidity. The sample dimensions, burials and removals correspond to the earth burial. The compost, based on green wastes, originates from the post-fermentation phase of the composting system Watenbüttel (Braunschweig). The results are to be seen in Fig. 4.

In the diagrams the mass loss is entered against the time (in weeks). In earth burial the copolyesters PTA(39/61) and PTS(41/59), with lower proportions of terephthalic acid, can no longer be isolated after 7 - 8 weeks. PTS(43/57) after this time has a weight loss of 14%. No weight loss in earth burial at ambient temperature was shown by PTS(56/44). Example 10 shows that at ambient temperature during the period investigated there is no

hydrolytic influence for the polyesters tested. Thus one can speak of microbial decomposition.

During the composting at 60°C, all the polyesters produced in Examples 1 - 4 show decomposition. In this case the PTA copolyesters with adipic acid as an aliphatic dicarboxylic acid component can no longer be isolated after 6 - 7 weeks. The copolyesters with sebacic acid as an aliphatic dicarboxylic acid component reveal significant weights losses (PTS(11/59) about 40%, PTS(56/44) about 20% after 10 weeks). Example 10 shows that the hydrolytic influence at 60°C fulfils a function reinforcing microbial decomposition. With adipic acid as an aliphatic dicarboxylic acid component this influence is more marked than with sebacic acid as an aliphatic dicarboxylic acid component. By appropriate choice of the monomer components and of the stoichiometry of the statistical copolyesters, thus made-to-measure polyesters can be represented as regards decomposition speed and material properties.

Example 12

Synthesis and decomposition of model Oligomers of poly(trimethylene terephthalate) (PTMT)

0.131 mol propanediol, 0.131 mol DMT and 0.04 g zinc acetate dihydrate are condensed with respectively 20, 50 and 100 mol% excess of 1,3-propanediol in the melt at 210°C under a nitrogen atmosphere and at normal pressure.

The oligomers are ground, successively washed with water and diethyl ether and dried for 24h in vacuum. The aromatic oligomers listed in Table 3 result.

Decomposition of the oligomers is tested in a modified Sturm test. The PTMT oligomers are the sole source of carbon. 1 vol-% of a compost eluate serves as a decomposition culture, and a mineral salt medium according to DIN 53739C as a nutrient source. The experiment is carried out at 25°C, with an air supply of about 2 l/h and in 100 ml liquid volume.

While the oligomer fractions with $n < 3$ are subject to extensive microbial decomposition, fractions with $n \geq 3$ reveal no decomposition by micro-organisms. The results are shown in Fig. 7.

Example 13

Synthesis and decomposition of model oligomers of poly(ethylene terephthalate) (PET)

0.161 mol 1,2-ethanediol, 0.161 mol DMT and 0.04 g zinc acetate dihydrate are condensed with 100 mol-% excess of 1,2-ethanediol in the melt at 210°C, in a nitrogen atmosphere and at normal pressure. The oligomer is ground, successively washed with water and diethyl ether, and dried for 24 h in vacuum.

Biological decomposition was tested as in Example 12, and gives similar results.

Example 14

Synthesis and decomposition of model oligomers of polytetraethylene terephthalate) (PBT)

0.111 mol 1,4-butanediol, 0.111 mol DMT and 0.04 g zinc acetate dihydrate are condensed with 100 mol-% excess of 1,4-butanediol in the melt at 210°C in a nitrogen atmosphere and at normal pressure. The oligomer is ground, successively washed with water and diethyl ester, and dried for 24 h in vacuum.

The biological decomposition occurs as described in Example 12, and gives similar results.

Fig 8

1. Flat material, individual filaments, filamentary material of moulded parts of biodegradable polyester, which are degraded in the natural environment by the action of micro-organisms, the polyester being produced from 1,4-butanediol or 2,3-butanediol as aliphatic polyol and an aromatic compound and simultaneously adipic acid as an aliphatic dicarboxylic acid as a monomer component, and characterised in that that the aromatic compound is terephthalic acid and the polyester has constitutional repeater units or returning units, which

(1) on the one hand consist of polyol and aromatic polycarboxylic acid and

(11) on the other hand consist of polyol and aliphatic polycarboxylic acid,

more than 90% by weight of the units according to (1) being directly linked with none, or at least with one further unit according to (1), and the polyester having a proportion, ascribable to terephthalic acid as aromatic dicarboxylic acid as a monomer component, of 35 to 65 mol-% (relative to overall acid content).

2. Flat material, individual filaments, filamentary material of moulded parts according to claim 1, characterised in that the polyester has a molecular weight (M_w , determined via GPC, relative to polystyrol standard), of 1000 to 70000 g/mol.

3. Flat material, individual filaments, filamentary material of moulded parts according to claim 1,

Amended

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characterised in that the polyester has a melting point of 40 to 150°C and especially 90 to 150°C.

4. Flat material, individual filaments, filamentary material or moulded parts according to one of the preceding claims, in the form of films as flat material or injection moulded, extruded or foamed moulded parts.

5. Filamentary material according to claim 1, in the form of fibres, felt or textiles.

6. Flat material, individual filaments, filamentary material or moulded parts according to claim 1 as a composite material.

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ABSTRACT

The invention relates to a biodegradable polyester (particularly in the form of a raw material or work material), which is degraded in a natural environment under the action of micro-organisms, for example according to DIN 53739D or ASTM D5338-92, the polyester being characterised in that the polyester has been produced from an aliphatic polyol and an aromatic polycarboxylic acid and at the same time from an aliphatic polycarboxylic acid as a monomer component, and has constitutional repeater units or returning units which

(1) on the one hand consist of polyol and aromatic polycarboxylic acid and

(2) on the other hand of polyol and aliphatic polycarboxylic acids,

more than 90% of the units according to (1) being directly linked with none or with at most one further unit according to (1).

Patent Claims

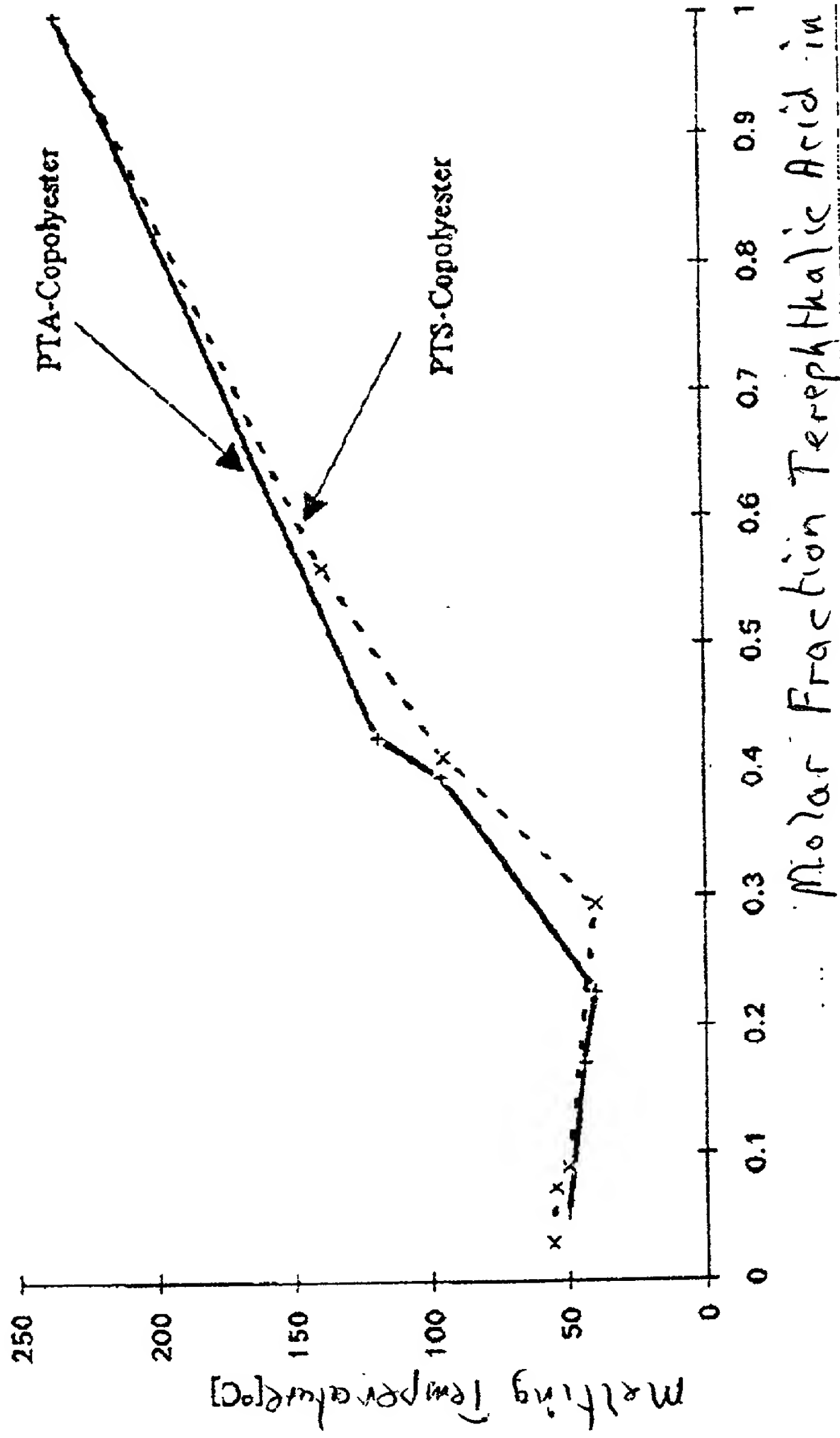


Abb. 1: Melting points of statistical copolyesters on the basis of 1,3-propane diol, in dependence on molar fraction with terephthalic acid in the acid proportion.

Abb. 2: Decomposition in the aquatic system in dependence on the proportion of terephthalic acid.

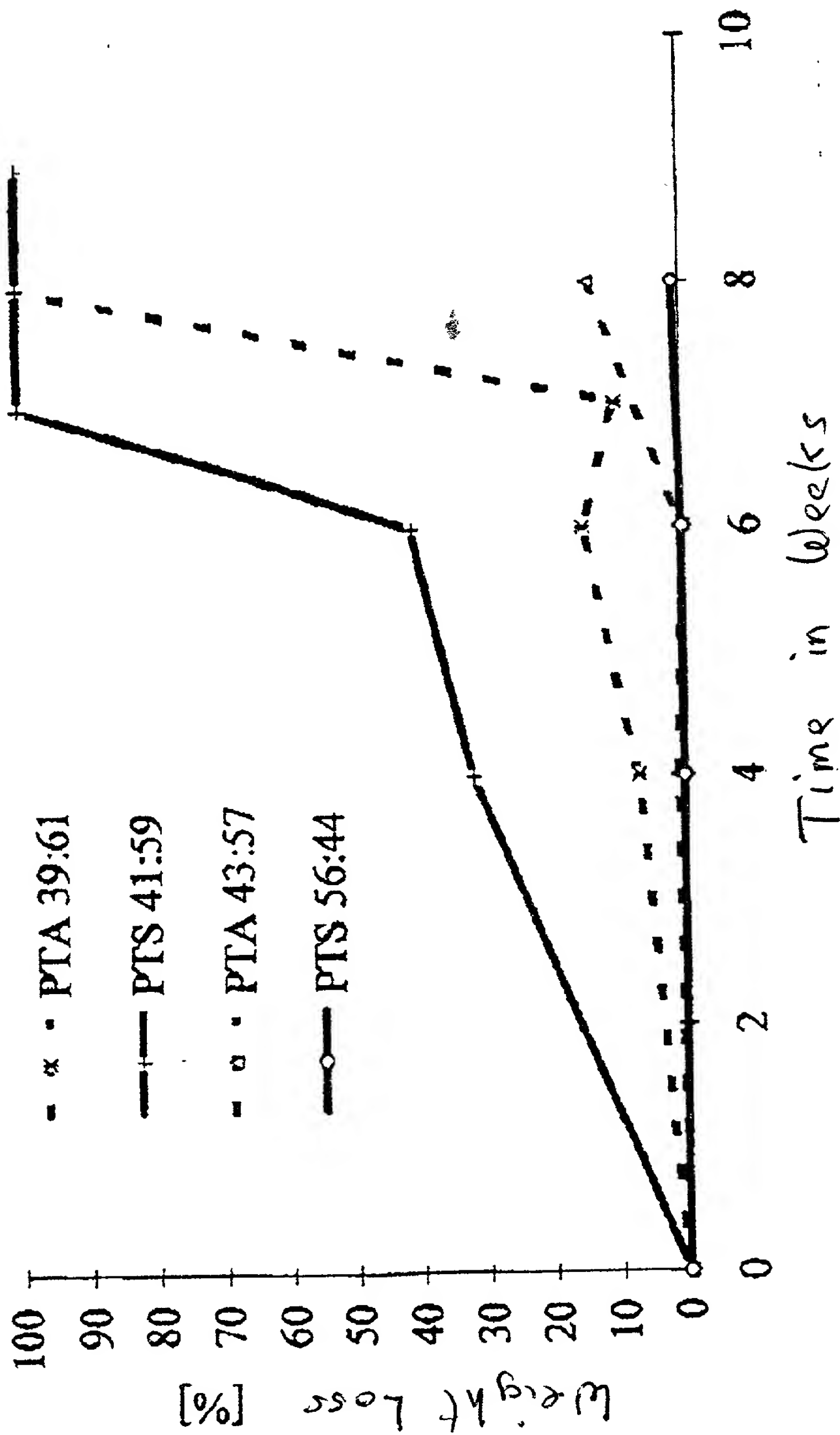


Abb. 3: Biological decomposition (as weight loss) in Soil Burial in dependence on the incubation time.

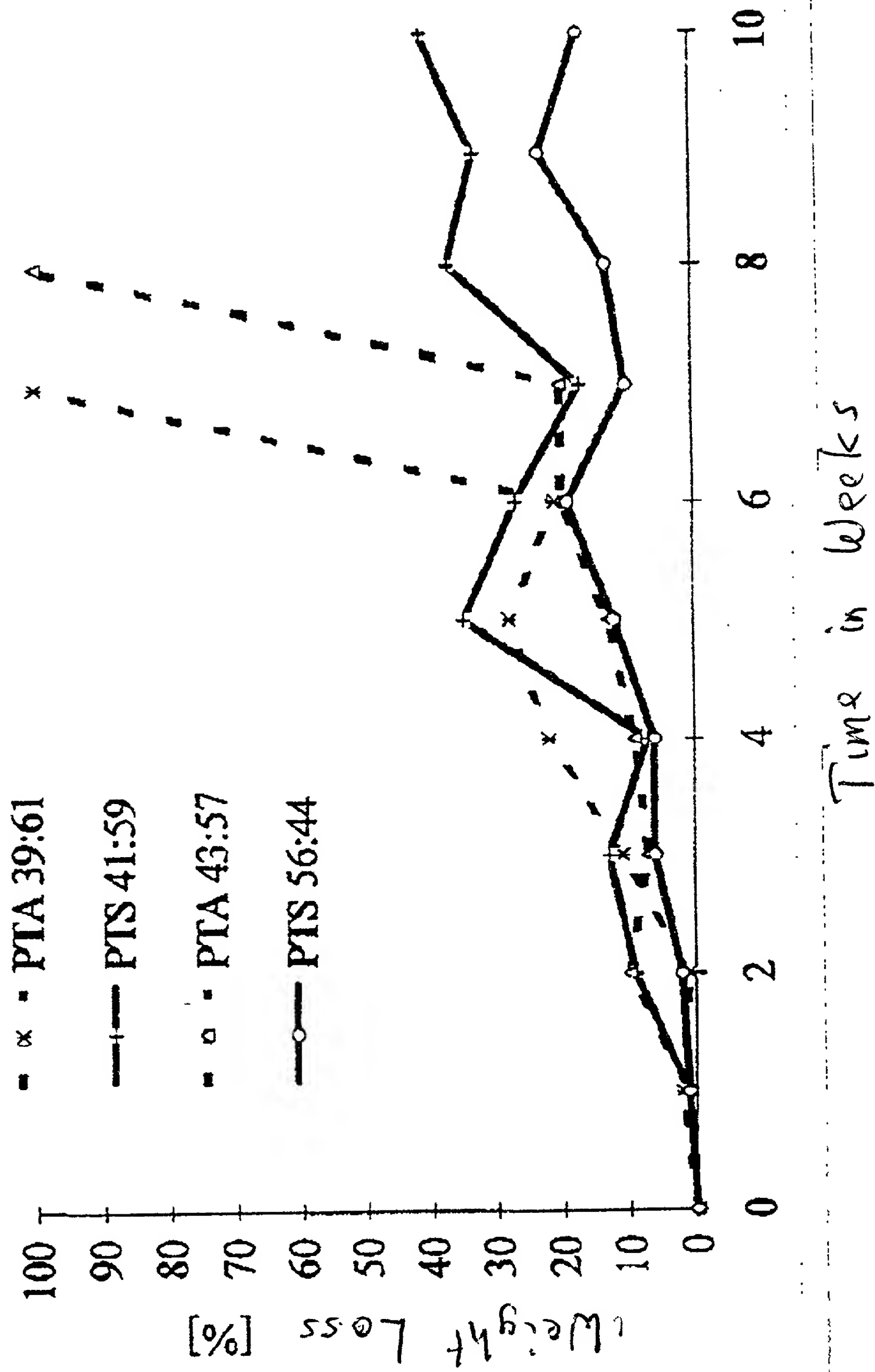


Abb. 4: Weight loss with composting at 60°C

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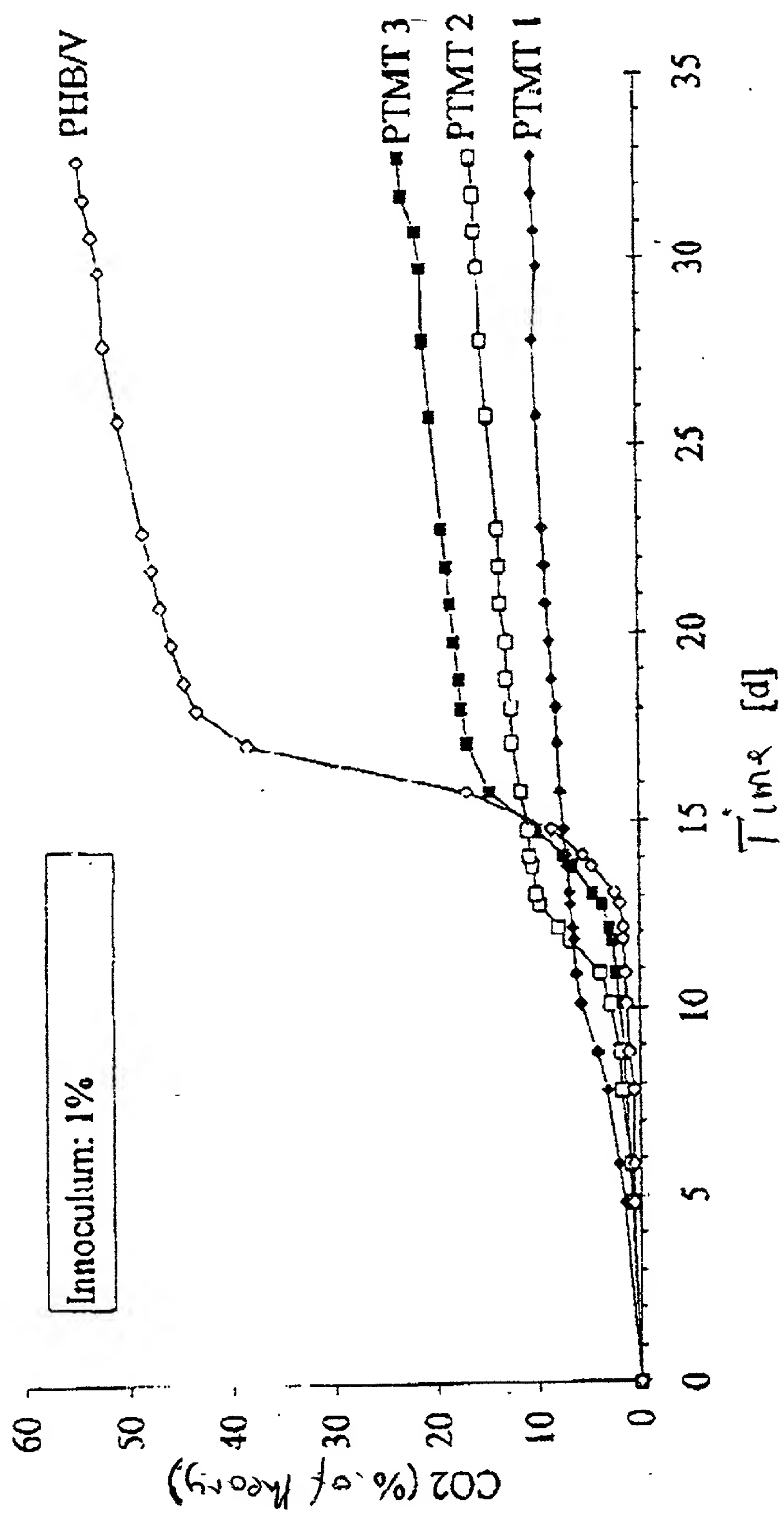


Abb. 5: CO₂-development during PTMT-Oligomers in the modified Sturm test!
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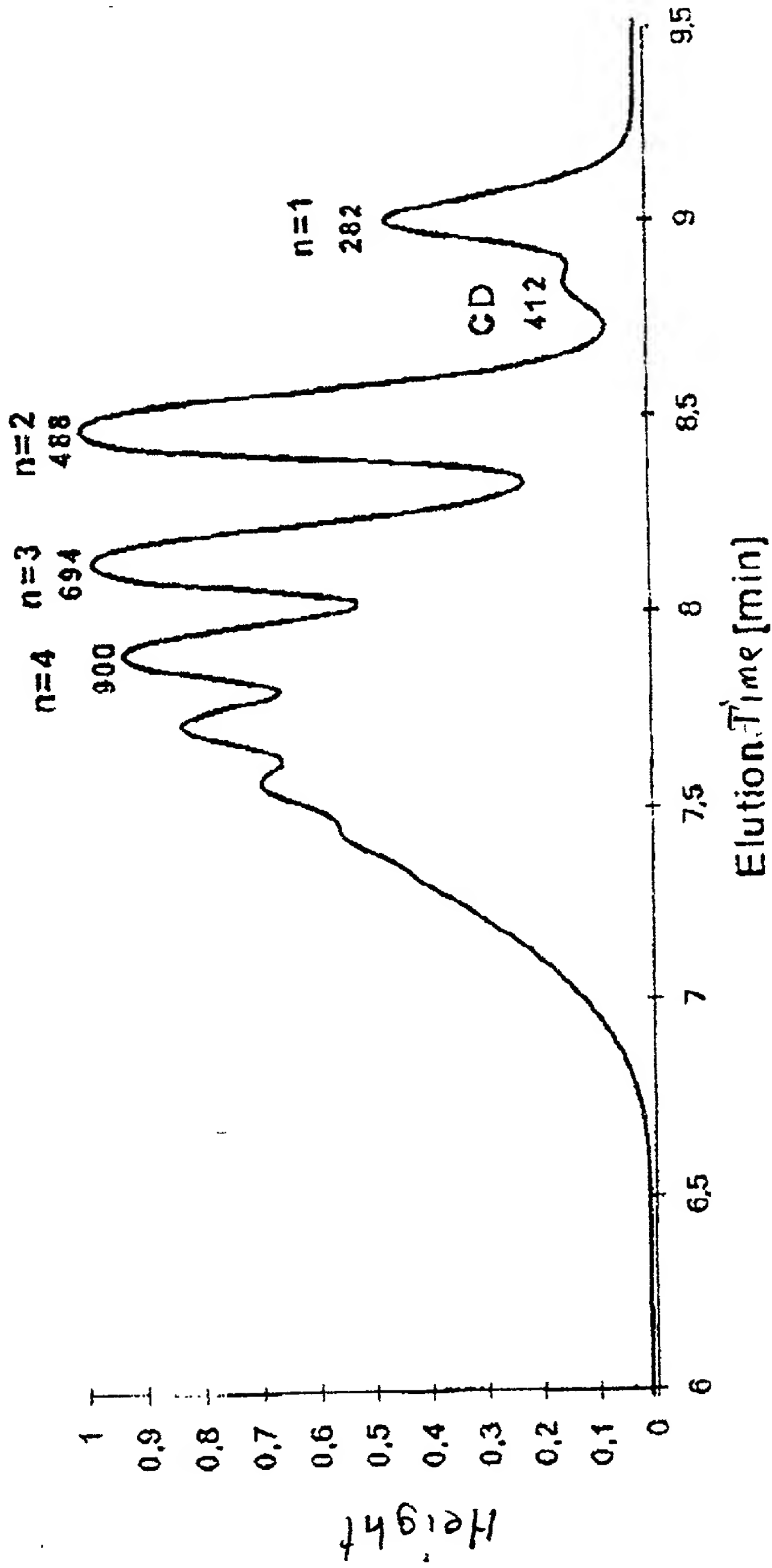
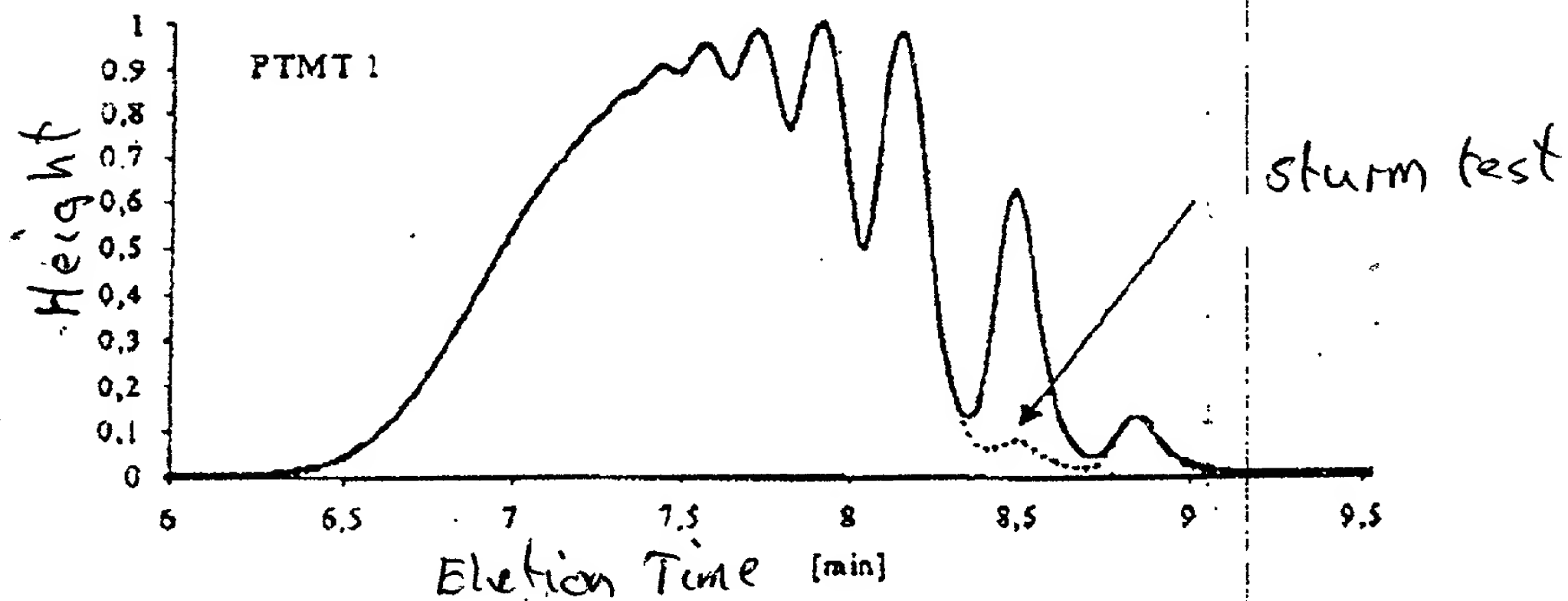
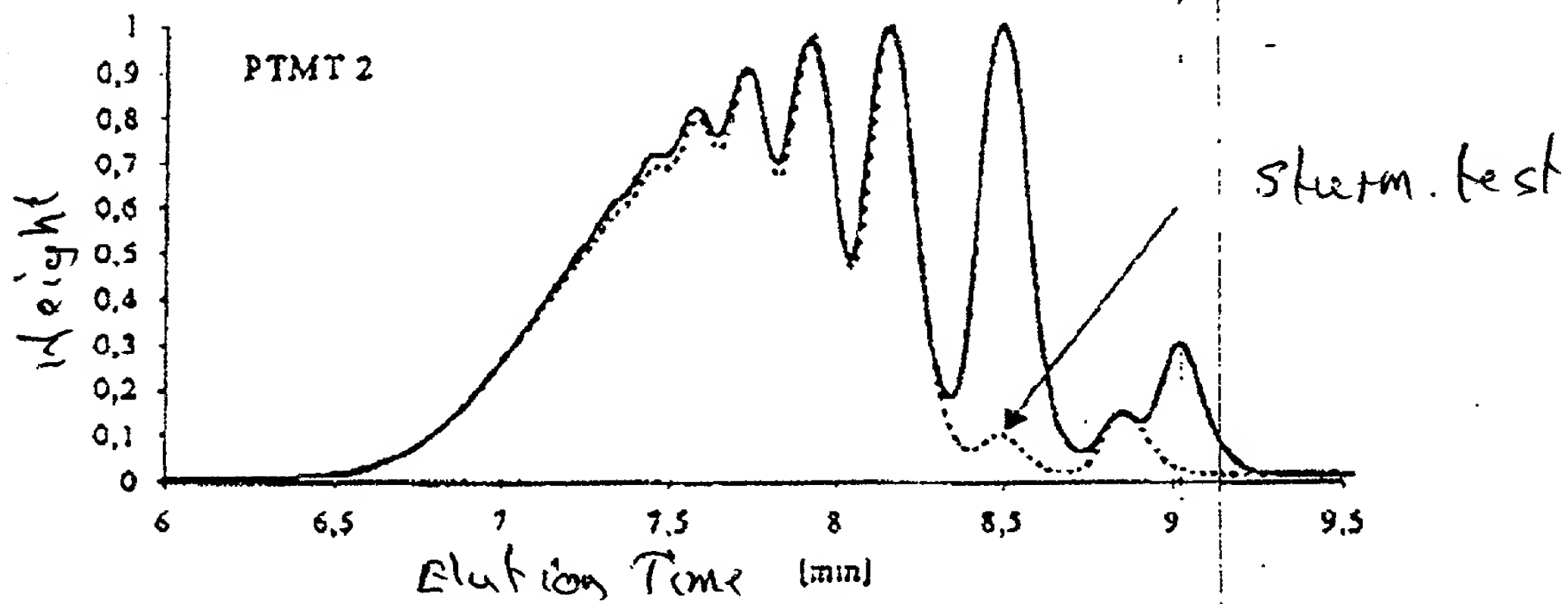
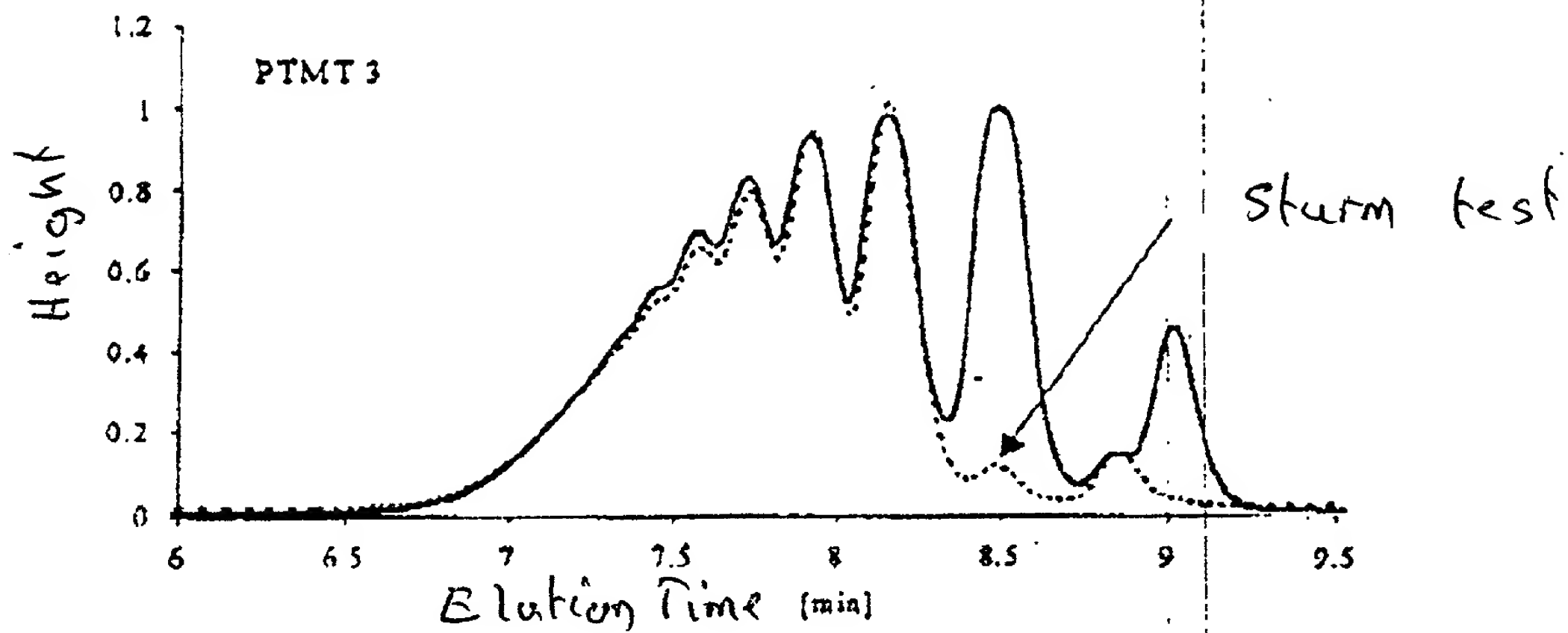


Abb. 6: PTMT 3 - GPC-Chromatogramm with association of the polycondensation products



bb.7: GPC-Chromatograms before and after decomposition of the aromatic oligomer PTMT 1-3

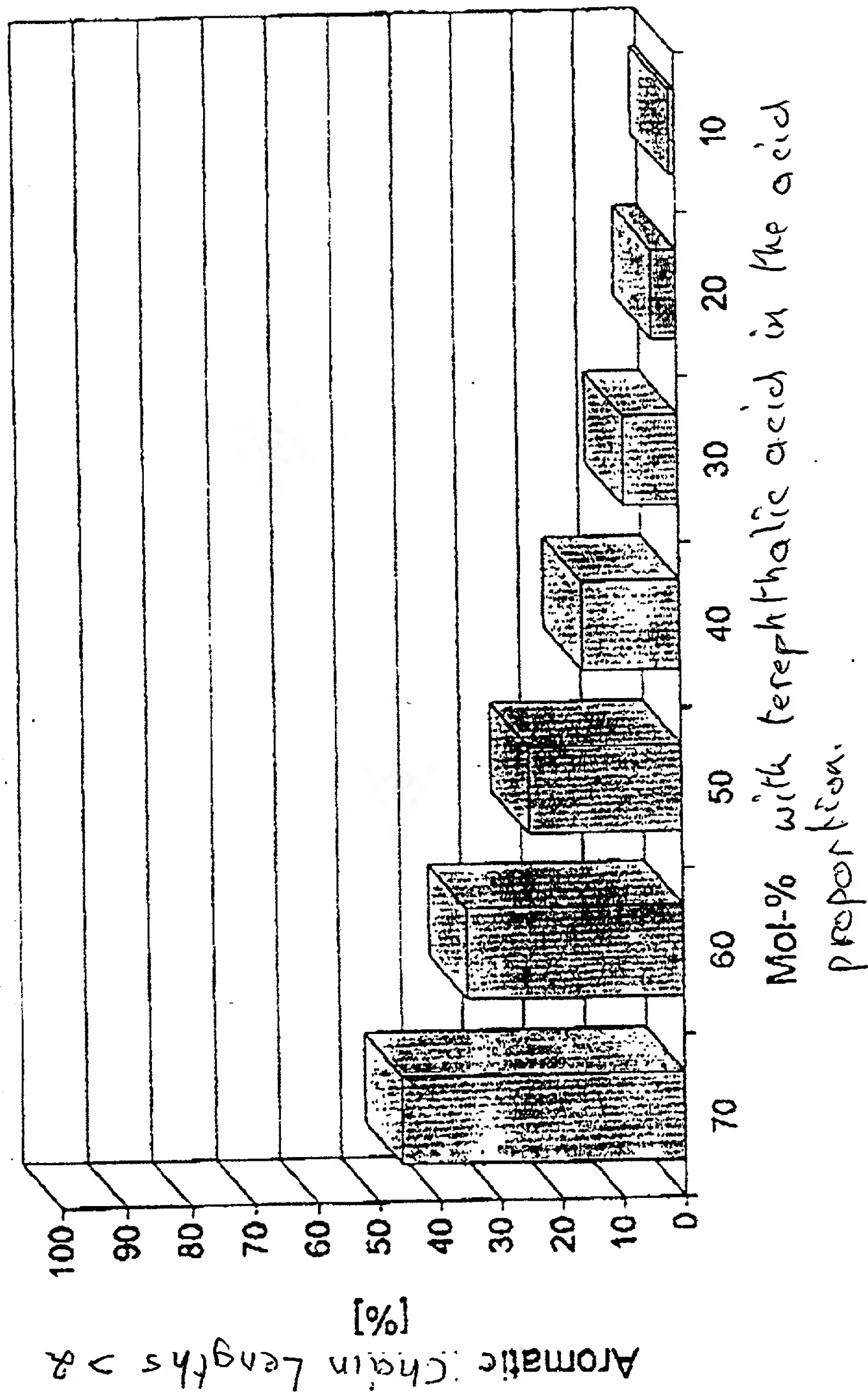


Abb. 8: Proportion of aromatic sequences with $n \geq 2$ in dependence on the T proportion

PCT/EP 95/02 722

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Biologically degradable polyester and working material consistingthe specification of which **thereof**(check one) ☐ is attached hereto.☐ was filed on _____ as

Application Serial No. _____

and was amended on _____

(if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

COUNTRY	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED
Germany	44 32 161.9	09 09 1994	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
Germany	(1)95 08 737.2	10 03 1995	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

APPLICATION NUMBER	DATE OF FILING (day, month, year)	STATUS (patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. Joseph C. Sullivan, Registration No. 18,720; John Kurucz, Registration No. 18,688; Gerald Levy, Registration No. 24,419; Joseph T. Eisele, Registration No. 25,331; Ronald R. Santucci, Registration No. 28,988; William H. Dippert, Registration No. 26,723; Tiberiu Weisz, Registration No. 29,876; Ronald E. Brown, Registration No. 32,200 and John Gulbin, Registration No. 33,180. I (we) further authorize my (our) attorney to insert the proper serial number and filing date awarded to my (our) application on this document, above my (our) signature(s).

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	RESIDENCE & CITIZENSHIP	CITY <u>Braunschweig</u>	STATE OR FOREIGN COUNTRY <u>FRG</u>
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200	FULL NAME OF INVENTOR	FAMILY NAME <u>Mueller</u>	FIRST GIVEN NAME <u>Rolf-Joachim</u>
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	POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>Mascheroder Weg 1, 38124 Braunschweig</u>	
300 203	FULL NAME OF INVENTOR	FAMILY NAME <u>Deckwer</u>	FIRST GIVEN NAME <u>Wolf-Dieter</u>
	RESIDENCE & CITIZENSHIP	CITY <u>Braunschweig</u>	STATE OR FOREIGN COUNTRY <u>FRG</u>
	POST OFFICE ADDRESS	POST OFFICE ADDRESS <u>Mascheroder Weg 1, 38124 Braunschweig</u>	

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

SIGNATURE OF INVENTOR 201 <u>Uwe Witt</u>	SIGNATURE OF INVENTOR 202 <u>Rolf-Joachim Mueller</u>	SIGNATURE OF INVENTOR 203 <u>Wolf-Dieter Deckwer</u>
DATE <u>08.08.1995</u>	DATE <u>08.08.1995</u>	DATE <u>08.08.1995</u>

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant or Patentee: WNO WITZ, et al. Attorney's Docket No. BOET 0103 PUSA
 Serial or Patent No.: PCT/EP/02722
 Filed or Issued: July 12, 1995
 For: BIOLOGICALLY DEGRADABLE POLYESTER AND WORKING MATERIAL CONSISTING THEREOF

VERIFIED STATEMENT (DECLARATION) CLAIMING SMALL ENTITY STATUS
 (37 CFR 1.9(f) and 1.27(c)) - SMALL BUSINESS CONCERN

I hereby declare that I am

- ☐ the owner of the small business concern identified below;
☒ an official of the small business concern empowered to act on behalf of the concern identified below:

NAME OF CONCERN GESELLSCHAFT FÜR BIOTECHNOLOGISCHE FORSCHUNG mbH (GFB)

ADDRESS OF CONCERN Mascheroder Weg 1, D-38124 Braunschweig, GERMANY

I hereby declare that the above-identified small business concern qualifies as a small business concern as defined in 13 CFR 121.3-10, and reproduced in 37 CFR 1.9(d), for purposes of paying reduced fees under section 41(a) and (b) of Title 35, United States Code, in that the number of employees of the concern, including those of its affiliates, does not exceed 500 persons. For purposes of this statement, (1) the number of employees of the business concern is the average over the previous fiscal year of the concern of the persons employed on a full-time, part-time or temporary basis during each of the pay periods of the fiscal year, and (2) concerns are affiliates of each other when either, directly or indirectly, one concern controls or has the power to control the other, or a third party or parties controls or has the power to control both.

I hereby declare that rights under contract or law have been conveyed to and remain with the small business concern identified above with regard to the invention, entitled BIOLOGICALLY DEGRADABLE POLYESTER AND WORKING MATERIAL CONSISTING THEREOF

by inventor(s) described in

- ☒ the specification filed herewith
 application PCT/EP95/02722 filed July 12, 1995
 patent no. Issued

The rights held by the above-identified small business concern are exclusive.

I acknowledge the duty to file, in this application or patent, notification of any change in status resulting in loss of entitlement to small entity status prior to paying, or at the time of paying the earliest of the issue fee or any maintenance fee due after the date on which status as a small entity is no longer appropriate. (37 CFR 1.28(b))

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application, any patent issuing thereon, or any patent to which this verified statement is directed.

NAME OF PERSON SIGNING Prof. Dr. G. Maess Dr. G. Frischmann

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